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Molecular Engineering of Liquid Crystalline Polymers by Living Polymerization. 22.
Synthesis and Characterization of Binary Copolymers of 11-[4-Cyano-4'-biphenyl)oxy]
undecanyl Vinyl Ether with (2S, 3S)-(+)-2-Chloro-3-Methylpentyl-4'-(8-Vinyloxyoctyloxy)
biphenyl-4-carboxylate and of (2S, 3S)-(+)-2-Chloro-3-Methylpentyl-4'-(8-Vinyloxy
octyloxy)biphenyl-4-Carboxylate with 3-[4-Cyano-4'-biphenyl)oxy]propyl Vinyl Ether

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The synthesis and characterization of poly{11-[(4-cyano-4'-biphenyl)oxy]undecanyl vinyl ether-co-(2S,3S)-(+)-2-chloro-3-methylpentyl 4'-(8-vinyloxyoctyloxy)biphenyl-4-carboxylate}X/Y {poly[(6-11)-co-(15-8)]X/Y} (where X/Y represents the molar ratio of the two structural units) and poly{(2S,3S)-(+)-2-chloro-3-methylpentyl 4'-(8-vinyloxyoctyloxy)biphenyl-4-carboxylate-co-3-[(4-cyano-4'-biphenyl)oxy]propyl vinyl ether}X/Y {poly[(15-8)-co-(6-3)]X/Y} with degree of polymerization of about 20 and molecular weight distribution of about 1.1 are described. The mesomorphic behavior of all copolymers determined from both first, second and subsequent differential scanning calorimetric (DSC) scans was discussed as a function of composition. As determined from the second DSC scans, poly(6-11) exhibits enantiotropic smectic A (s_A) and s_X (unidentified smectic), poly(6-3) enantiotropic nematic mesophases, while poly(15-8) exhibits enantiotropic s_A, chiral smectic C (s_C^*) and s_X (unidentified smectic) mesophases. Poly[(6-11)-co-(15-8)]X/Y exhibit a s_A phase over the entire range of compositions. This mesophase displays a continuous dependence of copolymer composition with an upward curvature. Poly[(15-8)-co-(6-3)]X/Y with X/Y from 10/0 to 3/7 displays an enantiotropic s_A mesophase as their highest phase, while those with X/Y from 2/8 to 1/9 an enantiotropic cholesteric mesophase.

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ABSTRACT

The synthesis and characterization of poly{11-[(4-cyano-4'-biphenyl)oxy]undecanyl vinyl ether-co-(2S,3S)-(+)-2-chloro-3-methylpentyl 4'-(8-vinyloxyoctyloxy)biphenyl-4-carboxylate}X/Y {poly[(6-11)-co-(15-8)]X/Y} (where X/Y represents the molar ratio of the two structural units) and poly{(2S,3S)-(+)-2-chloro-3-methylpentyl 4'-(8-vinyloxyoctyloxy)biphenyl-4-carboxylate-co-3-[(4-cyano-4'-biphenyl)oxy]propyl vinyl ether}X/Y {poly[(15-8)-co-(6-3)]X/Y} with degree of polymerization of about 20 and molecular weight distribution of about 1.1 are described. The mesomorphic behavior of all copolymers determined from both first, second and subsequent differential scanning calorimetric (DSC) scans was discussed as a function of composition. As determined from the second DSC scans, poly(6-11) exhibits enantiotropic smectic A (s_A) and s_X (unidentified smectic), poly(6-3) enantiotropic nematic mesophases, while poly(15-8) exhibits enantitropic s_A, chiral smectic C (s_C*) and s_X (unidentified smectic) mesophases. Poly[(6-11)-co-(15-8)]X/Y exhibit a s_A phase over the entire range of compositions. This mesophase displays a continuous dependence of copolymer composition with an upward curvature. Poly[(15-8)-co-(6-3)]X/Y with X/Y from 10/0 to 3/7 displays an enantitropic s_A mesophase as their highest phase, while those with X/Y from 2/8 to 1/9 an enantiotropic cholesteric mesophase.

INTRODUCTION

Copolymerization provides the most effective method for the molecular engineering of side chain liquid crystalline polymers.[1,2] Copolymerization of monomer pairs each containing mesogenic units[1-10] can be classified into at least four different groups: (1) copolymers from monomer pairs containing identical mesogens and polymerizable groups but different spacer lengths; (2) copolymers from monomer pairs containing identical

mesogens and spacer lengths but different polymerizable groups; (3) copolymers from monomer pairs containing dissimilar mesogens but either similar or different spacer lengths and polymerizable groups; (4) copolymers from monomer pairs containing constitutional isomeric units and similar or dissimilar spacers and polymerizable groups.[2]

For a quatitative approach to the understanding of side chain liquid crystalline copolymers, molecular weight, molecular weight distribution and copolymer composition should be well defined.[11] Copolymers synthesized by chain copolymerization reactions exhibit a heterogenuous composition since the copolymer composition differs from that of the monomer feed in the initial reaction mixture, exception being the azeotropic copolymerizations. Futhermore, the temperature and the nature of the mesophase are molecular weight[12-16] and molecular weight distribution dependent.[15,17] Therefore, for a quantitative investigation of side chain liquid crystalline copolymers it is essential that these factors are well defined . The ideal solution to the synthesis of copolymers by chain reactions would be to select monomer pairs that can be copolymerized by an azeotropic living mechanism.[18]

Several previous publications[19,20] from our laboratory have investigated the first series of quantitative experiments on statististical binary copolymers with well defined composition, molecular weight and molecular weight distribution by living cationic polymerization corresponding to class 1, i.e., copolymers from monomer pairs containing identical mesogenic units and polymerizable groups but different spacer lengths. The general trend observed from these investigations is that over the entire range of copolymer compositions where the two structural units of the copolymer are isomorphic within a certain mesophase, both the phase transition temperatures and the enthalpy changes associated with this mesophase follow a continuous dependence of copolymer composition. The dependence of isotropization temperature on composition can also be

predicted by the Schroeder-van Laar equation[21] when the isomorphic structural units of the copolymer behave like an ideal solution of these structural units.[19,20] When the two structural units are non-isomorphic within at a certain composition, a continuous dependence of both transition temperatures and enthalpy changes with a triple point at a certain copolymer composition can be observed.[19b-e]

Presently, we are investigating the copolymers based on monomer pairs containing dissimilar mesogens and dissimilar spacer lengths but identical polymerizable groups which correspond to the class of copolymers 3. In the case of different chemical structure for each mesogen, the components of such polymer blends are generally immiscible and attempts to obtain homogenuous mixtures were not successful.[6] Copolymers from this class are however of interest for the fundamental understanding of phase diagrams obtained by copolymerization.

This paper will describe the synthesis and characterization of two copolymer series based on 11-[(4-cyano-4'-biphenyl)oxy]undecanyl vinyl ether (6-11) and 3-[(4-cyano-4'-biphenyl)oxy]propyl vinyl ether (6-3) with poly{(2S,3S)-(+)-2-chloro-3-methylpentyl 4'-(8-vinyloxyoctyloxy)biphenyl-4-carboxylate} (18-5). All copolymers were synthesized with a degree of polymerization of 20 and different compositions. When the mesomorphic phases exhibited by the parent homopolymers with a degree of polymerization of about 20 are determined from the second heating scans, poly(6-11)[16a] exhibits enantitropic s_A and s_X, poly(6-3)[16b] enantiotropic nematic, and poly(15-8)[20c] enantiotropic s_A, s_C^* and s_X mesophases. Therefore, it is expected that the investigation of these two series of copolymers will provide information about the phase behavior of the copolymers containing different mesogens and different spacer lengths derived from pairs of homopolymers exhibiting as the high temperature mesophases, s_A and s_A, and

respectively, n and s_A. Therefore, this investigation will provide a quantitative understanding of the class of copolymers 3.

EXPERIMENTAL

Materials

All materials were commercially available and were used as received or purified as described previously.[16a,b] Methyl sulfide (anhydrous, 99%, Aldrich) was refluxed over 9-borabicyclo[3.3.1]nonane (9-BBN, crystalline, 98%, Aldrich) and then distilled under argon. Dichloromethane (99.6%, Aldrich) used as a polymerization solvent was first washed with concentrated sulfuric acid, then with water, dried over anhydrous magnesium sulfate, refluxed over calcium hydride and freshly distilled under argon before each use. Trifluoromethane sulfonic acid (triflic acid, 98%, Aldrich) was distilled under argon.

Techniques

^{1}H-NMR (200 MHz) spectra were recorded on a Varian XL-200 spectrometer. TMS was used as internal standard. A Perkin Elmer DSC-4 differential scanning calorimeter equipped with a TADS 3600 data station was used to determine the thermal transitions which were reported as the maxima and minima of their endothermic and exothermic peaks respectively. In all cases, heating and cooling rates were 20°C/min unless otherwise specified. Glass transition temperatures (Tg) were read at the middle of the change in the heat capacity. For certain polymer samples, the first heating scans sometimes differ from the second and subsequent heating scans. However, the second and subsequent heating scans are identical. The first heating scans can be reobtained after proper thermal treatment of the polymer sample. A Carl-Zeiss optical polarized microscope (magnification: 100x) equipped with a Mettler FP 82 hot stage and a Mettler FP 800 central

processor was used to observe the thermal transitions and to analyze the anisotropic textures.[22,23] Molecular weights were determined by gel permeation chromatography (GPC) with a Perkin Elmer series 10 LC instrument equipped with LC-100 column oven, LC-600 autosampler and a Nelson analytical 900 series integrator data station. The measurements were made at $40^{\circ}C$ using the UV detector. A set of Perkin Elmer PL gel columns of 10^4 and 500 Å with $CHCl_3$ as solvent (1ml/min) and a calibration plot constructed with polystyrene standards was used to determine the molecular weights. Therefore, all molecular weights discussed in this paper are relative to polystyrene. High pressure liquid chromatography (HPLC) experiments were performed with the same instrument.

Synthesis of Monomers

11-[(4-Cyano-4'-biphenyl)oxy]undecanyl vinyl ether (6-11),[16a] 3-[(4-cyano-4'-biphenyl)oxy]propyl vinyl ether (6-3)[16b] and (2S,3S)-(+)-2-chloro-3-methylpentyl 4'-(8-vinyloxyoctyloxy)biphenyl-4-carboxylate (15-8)[20c] were synthesized and purified as described in previous publications. Their purity was higher than 99% (HPLC). Their detailed characterization was described in the previous publications.

Cationic Polymerizations and Copolymerizations

Polymerizations were carried out in glass flasks equipped with teflon stopcocks and rubber septa under argon atmosphere at $0^{\circ}C$ for 1 hr. All glassware was dried overnight at $130^{\circ}C$. The monomer was further dried under vacuum overnight in the polymerization flask. Then the flask was filled with argon, cooled to $0^{\circ}C$ and the methylene chloride, dimethyl sulfide and triflic acid were added via a syringe. The monomer concentration was about 10 wt% of the solvent volume and the dimethyl sulfide concentration was 10 times

larger than that of the initiator. The polymer molecular weight was controlled by the monomer/initiator ($[M]_0/[I]_0$) ratio. After quenching the polymerization with ammoniacal methanol, the reaction mixture was precipitated into methanol. When necessary, the polymers were reprecipitated until their GPC traces showed complete absence of unreacted monomers. Tables I and II summarize the polymerization results. Although polymer yields are lower than expected due to losses during the purification process, conversions determined by GPC analysis before polymer purification were almost quantitative in all cases.

RESULTS AND DISCUSSION

The synthesis, characterization and living polymerization of 11-[(4-cyano-4'-biphenyl)oxy]undecanyl vinyl ether (6-11),[16a] 3-[(4-cyano-4'-biphenyl)oxy]propyl vinyl ether (6-3)[16b] and (2S,3S)-(+)-2-chloro-3-methylpentyl 4'-(8-vinyloxyoctyloxy)biphenyl-4-carboxylate (15-8)[20c] were described previously. Scheme I outlines the synthesis of copolymers. The initiating system $CF_3SO_3H/S(CH_3)_2$[24,25] is known to induce living cationic polymerizations in CH_2Cl_2 at 0°C. The copolymerization results are listed in Tables I and II. The yields reported in Tables I and II are lower than quantitative due to polymer losses during the purification process. However, the conversions were quantitative and therefore, the copolymer composition is identical to that of the monomer feed (determined by 200 MHz ^{1}H-NMR spectroscopy). Figure 1 presents a typical 200 MHz ^{1}H-NMR spectrum of the aromatic region of poly[(15-8)-co-(6-3)]5/5 with its proton assignments. The ratio between the integrals of the signal at 6.95 ppm and 8.10 ppm was used to confirm the copolymer compositions. Therefore, these copolymerization systems follow an azeotropic pattern (i.e., $r_1=r_2=1.0$).

The GPC traces of all copolymers show a monomodal molecular weight distribution characterized by a polydispersity of about 1.15 (Tables I and II). Attempts were made to synthesize all copolymers with degrees of polymerization of about 20.

We have investigated the following two copolymer systems: poly[(6-11)-co-(15-8)]X/Y based on a monomer pair whose parent homopolymers exhibit enantiotropic s_A phases as their highest temperature mesophases and poly[(8-15)-co-(6-3)]X/Y based on a monomer pair whose parent homopolymers exhibit enantiotropic s_A and enantiotropic nematic phases as their highest temperature mesophases.

Poly[(6-11)-co-(15-8)]X/Y

The synthesis and characterization of poly[(6-11)-co-(15-8)]X/Y copolymers are summarized in Table I. The first and the second heating, and the first cooling DSC traces of all polymers and copolymers are presented in Figure 1a-c. As determined from the first DSC heating scans, poly(6-11)[16a] with a degree of polymerization of 19 exhbits an enantitropic s_A mesophase and a crystalline melting. When the phase behavior of the same poly(6-11) is determined from the second and subsequent heating DSC scans, it exhbits enantitropic s_A and s_X (unidentified smectic) mesophases. Regardless of the thermal history of the sample, poly(15-8)[20c] with a degree of polymerization of 18 exhibits enantitropic s_A, s_C^* and s_X mesophases (Figure 2a-c).

Let us first investigate the phase behavior of poly[(6-11)-co-(15-8)]X/Y as obtained from the first heating DSC scans (Figure 2a). The nature of the mesophase displayed by various copolymers is presented on this figure. Upon copolymerization, the temperature associated with the s_A-isotropic phase transition increases and therefore, the s_A mesophase exhibits a continuous dependence of composition with an upward curvature as clearly observed from their DSC traces (Figure 2a). That is, the structural units of both poly(6-11)

and poly(15-8) are isomorphic within the s_A phase over the entire range of copolymer compositions.[26] However, this dependence shows a non-ideal solution like behavior since there is a significant deviation from what is expected for the same dependence predicted by the Schroeder-van Laar equation for an ideal solution resulting from the structural units of this copolymer (Figure 3b).[21] All poly[(6-11)-co-(15-8)]X/Y copolymers exhibit a crystalline phase, while copolymers with X/Y=6/4 to 9/1 exhibit an induced s_X phase. Both the ability to obtain copolymers exhibiting a s_A mesophase with enhanced thermal stability and an induced smectic phase from structural units derived from two homopolymers which both display a s_A phase are interesting results for which do not have a definitive explanation.

However, the following speculative explanation is suggested. The new s_X mesophase may result because these copolymers contains strong polar cyano and less polar chiral alkyl groups. It is well known from studies of low molar mass liquid crystals that the mixture of strong polar and less polar mesogens may induce a smectic mesophase or/and enhance the thermal stability of the smectic mesophase.[27-32] We can speculate that polar cyano groups form the antiparellel associations between polar molecules with overlapped aromatic rings, while less polar chiral alkyl groups form a smectic structure with monomolecular layers. Therefore, upon copolymerization, dipolar associations of polar mesogens will rapidly collapse and the layer spacing decreases down to the line corresponding to what would be expected for a monomolecular layer. Consequently, both structural units will form denser packing upon copolymerization. Morphological experiments are required to support this speculative explanation.

However, upon copolymerization, the chiral smectic C and s_X phases of poly(15-8) are suppressed up to copolymer compositions of X/Y=1/9 and X/Y=2/8, respectively. Figure 3a plots the phase transitions from the first heating DSC scan as a function of

copolymer composition. As we can observe from Figure 3a, the s_A phase shows a continuous dependence of composition with an upward curvature. In the second DSC heating scan (Figure 2b), the s_A mesophase exhibits again a continuous dependence with an upward curvature. However, copolymers with X/Y=2/8 to X/Y=7/3 exhibit an induced crystalline phase, while copolymers with X/Y=4/6 to X/Y=8/2 an induced enantiotropic s_X phase. Nevertherless, the transition temperatures associated with s_X and s_C^* phases of poly(15-8), and with the s_X phase of poly(6-11) decrease upon copolymerization. The cooling DSC traces of these copolymers are similar to those of the second DSC heating scans (Figure 2b,c). The data collected from the second heating DSC scans and the first cooling scans are plotted in Figure 3c,d. Figure 3e plots the dependence of the enthalpy change associated with the s_A-i phase transition from first and second heating DSC scans and i-s_A phase transition from first cooling scan as a function of copolymer composition. This plot also shows the continuous character of the dependence of the enthalpy change associated with this phase transition versus copolymer composition Finally, Figure 4 presents some representative textures characteristic for the s_A and s_X phases exhibited by poly[(6-11)-co-(15-8)]6/4.

These experimental results provide information on the isomorphism of two monomeric structural units derived from two different mesogens and spacer lengths within a smectic A phase. In contrast to binary copolymers based on structural units containing the same mesogen but different spacer lengths which are isomorphic within the same mesogen and behave as an ideal solution derived from the two structural units, structural units based on dissimilar mesogens are isomorphic but behave as a non-ideal solution.

Poly[(15-8)-co-(6-3)]X/Y

This copolymer is synthesized from a pair of monomers whose parent homopolymers exhibit different mesophases before isotropization, that is, the highest temperature mesophase of poly($\underline{15\text{-}8}$)[20c] is s_A, while that of poly($\underline{6\text{-}3}$)[16b] is nematic. In addition, it is expected that this copolymer will generate, at a certain composition, also a cholesteric mesophase since poly($\underline{15\text{-}8}$) contains a chiral moiety. The synthesis and characterization of the copolymers poly[($\underline{15\text{-}8}$)-co-($\underline{6\text{-}3}$)]X/Y are presented in Table II.

Let us first discuss the phase behavior obtained from the first DSC heating scans (Figure 5a). The s_X phase of poly($\underline{6\text{-}3}$) shows a linear dependence up to a value of X/Y=3/7. As expected, a cholesteric mesophase was induced in copolymers with X/Y=1/9 and 2/8. Copolymers with X/Y=4/6 to 6/4 exhibit the s_A and an induced crystalline phase, while copolymers with X/Y=7/3 to 10/0 exhibit the s_A, s_C^* and s_X mesophases. The interest in these copolymers has arised from their propensity to form cholesteric mesophase. It is well established that copolymerization of a monomer pair based on a monomer containing a chiral group with a monomer whose parent homopolymer exhibits a nematic mesophase generates cholesteric copolymers.[33-37]

Figure 5a plots all the phase transitions from the first heating DSC scans as a function of copolymer composition. As we can observed from Figure 6a, the nematic and cholesteric mesophases show a linear dependence of composition up to a value of X/Y=2/8. This indicates that the structural units of both poly($\underline{6\text{-}3}$) and poly($\underline{15\text{-}8}$) are isomorphic within the nematic and cholesteric phases over a certain range of copolymer compositions. In addition, the smectic A mesophase also shows a continuous character with an upward curvature over a certain range of copolymer composition which represents a similar behavior to that of poly[($\underline{6\text{-}11}$)-co-($\underline{15\text{-}8}$)]X/Y. In the second heating scan (Figure 5b), the induced crystalline and s_X phases do not appear. This is due to their close proximity to the glass transition temperature of the copolymers. Therefore, these two

phases form only when the polymers are precipitated from solution. If the polymer is redissolved and reprecipitated, these phases reappear. However, the s_A, nematic and cholesteric mesophases follow the same trend as the one observed in the first DSC heating scans (Figure 5a). The cooling DSC scans of these copolymers show the same trend as those of the second heating scan (Figure 5b,c). The data collected from the second DSC heating scans and the first cooling scans are plotted in Figure 6b,c. The enthalpy changes associated with the highest temperature mesophase of these copolymers (Table II) are plotted in Figure 6d as a function of copolymer composition. A representative texture of the cholesteric mesophase is presented in Figure 7.

The results obtained for the copolymers poly[(6-11)-co-(15-8)]X/Y show that the copolymerization of a monomer containing a chiral group with a monomer whose parent homopolymer exhibits a nematic mesophase provides a simple technique for the synthesis of copolymers exhibiting an enantiotropic cholesteric mesophase and exhibiting an enatitropic smectic A phase with enhaced thermal stability.

In conclusion, the results described in this paper have demonstrated that, when two structural units of a copolymer based on dissimilar mesogens are isomorphic within a certain mesophase, the transition temperature and enthalpy change associated this mesophase show a continuous dependence over the entire range of copolymer composition. However, the dependence of the temperature transitions of this mesophase on copolymer composition, behaves as that of a solution derived from these two structural units which exhibits a non-ideal behavior.

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SCHEME AND FIGURE CAPTIONS

Scheme I. Cationic copolymerization of 6-n with 15-8

Figure 1. The aromatic region of the 200 MHz ^{1}H-NMR spectrum of poly[(15-8)-co-(6-3)]5/5.

Figure 2. DSC traces displayed during the first heating scan (a), second heating scan (b), and first cooling scan (c) of poly(6-11), poly(15-8) and of [poly(6-11)-co-(15-8)]X/Y.

Figure 3. The dependence of phase transition temperatures on the composition of [poly(6-11)-co-(15-8)]X/Y copolymers: (a) data from first heating scan: O -Tg; ■-Tk; ◊ -Ts$_X$-s$_A$(s$_C$*); □-Ts$_C$*-s$_A$; □-Ts$_A$-i; (b) The dependence of s$_A$ -n and s$_A$-i phase transition temperatures on composition of poly[(6-11)-co-(6-5)]X/Y: (Δ) data calculated by Schroeder-van Laar equation; (□) experimental data from the first heating scan; (c) data from second heating scan: O -Tg; ■-Tk; ◊ -Ts$_X$-s$_A$(s$_C$*); □-Ts$_C$*-s$_A$; □-Ts$_A$-i; (d) data from first cooling scan: ● -Tg; ■-Tk; ◆ -Ts$_A$(s$_C$*)-s$_X$; □-Ts$_A$-s$_C$*; □-Ti-s$_A$; (e) The dependence of the enthalpy changes associated with the mesomorphic-isotropic and isotropic-mesomorphic phase transitions on the composition of [poly(6-11)-co-(15-8)]X/Y: □-ΔHs$_A$-i (data from first heating scan); Δ-ΔHs$_A$-i (data from second heating scan); O-ΔHi-s$_A$ (data from first cooling scan)

Figure 4. Representative optical polarized micrographs (100x) of: (a) [poly(6-11)-co-(15-8)]6/4 at 140 °C on the cooling scan (s_A phase); (b) [poly(6-11)-co-(15-8)]6/4 at 60 °C on the cooling scan (s_X phase)

Figure 5. DSC traces displayed during the first heating scan (a), second heating scan (b), and first cooling scan (c) of poly(15-8), poly(6-3) and of [poly(15-8)-co-(6-3)]X/Y.

Figure 6. The dependence of phase transition temperatures on the composition of [poly(15-8)-co-(6-3)]X/Y copolymers: (a) data from first heating scan: O -Tg; ■-Tk; ◊ -T_X-n(Ch); ◊ -Ts_X-s_A(s_C*); ⊡-s_C*-s_A; □-Ts_A-i; Δ-Tn(Ch)-i; (b) data from second heating scan: O -Tg; ◊ -Ts_X-s_A(s_C*); ⊡-s_C*-s_A; □-Ts_A-i; Δ-Tn(Ch)-i; (c) data from first cooling scan: ● -Tg; ♦ -Ts_A(s_C*)-s_X; ⊡-s_A-s_C*; □-Ti-s_A; Δ-Ti-n(Ch); (d) The dependence of the enthalpy changes associated with the mesomorphic-isotropic and isotropic-mesomorphic phase transitions on the composition of [poly(15-8)-co-(6-3)]X/Y: □-ΔHs_A-i (data from first heating scan); Δ-ΔHs_A-i (data from second heating scan); O-ΔHi-s_A (data from first cooling scan)

Figure 7. Representative optical polarized micrograph (100x) of: (a) [poly(15-8)-co-(6-3)]8/2 at 85 °C on the cooling scan (cholesteric phase).

Table I. Cationic Copolymerization of 6-11 with 15-8 (polymerization temperature, 0°C; polymerization solvent, methylene chloride; [M]o=[6-11]+[15-8]]=0.205-0.256M; [M]o/[I]o=20; [(CH3)2S]o/[I]o=10; polymerization time, 1hr) and Characterization of the Resulting Copolymers. Data on first line are from first heating and cooling scans. Data on second line are from second heating scan.

| Sample No.	[6-11]/[15-8] (mol/mol)	Polymer yield(%)	$Mn \times 10^{-3}$ GPC	Mw/Mn GPC	DP	phase transitions (°C) and corresponding enthalpy changes (kcal/mru) — heating	cooling
1	0/10	77	8.6	1.08	18	g 16.7 sx 55.2 (0.13) sC* 93.4 (0.17) sA 104.7 (1.10) i g 16.1 sx 53.7 (0.13) sC* 92.1 (0.15) sA 103.7 (0.96) i	i 95.7 (0.93) sA 86.3 (0.14) sC* 45.9 (0.12) sx 13.6 g
2	1/9	84	10.1	1.22	21	g 25.1 k 45.2 (0.41) sC* 89.1 (0.07) sA 130.8 (1.20) i g 24.4 sx 42.8 (0.15) sC* 88.9 (0.11) sA 129.9 (0.11) i	i 122.5 (1.23) sA 79.3 (0.11) sC* 32.9 (0.21) sx 19.8 g
3	2/8	77	8.8	1.10	19	g 33.3 k 49.5 (0.15) sC* 79.4(-) sA 141.7 (1.35) i g 32.5 k 52.9 (0.60) sC* 78.2 (-) sA 140.6 (1.26) i	i 132.7 (1.27) sA 66.2 (-) sC* 44.5 (0.64) k 25.4 g
4	3/7	91	10.2	1.11	22	k 51.3 (0.10) k 63.1 (0.99) sA 149.5 (1.36) i k 61.7 (0.80) sA 150.4 (1.23) i	i 141.9 (1.18) sA 52.7 (0.77) k
5	4/6	89	9.4	1.10	21	k 62.3 (0.13) k 74.2 (1.16) sA 158.9 (1.35) i k 74.4 (1.09) sA 158.9 (1.24) i	i 150.6 (1.21) sA 65.1 (1.01) k
6	5/5	88	8.5	1.09	19	k 59.9 (0.23) k 79.1 (1.05) sA 160.7 (1.39) i k 75.4 (-) sx 78.6 (1.16)a sA 160.8 (1.16) i	i 153.0 (1.19) sA 68.8 (1.17)a sx 61.2 (-)k
7	6/4	93	9.6	1.17	22	k 58.6 (0.39) k 76.7 (0.96) sA 163.7 (1.21) i k 69.5 (-) sx 77.1 (1.03)a sA 163.9 (1.06) i	i 155.9 (1.07) sA 67.1 (1.00) sx 55.8 (0.62) k
8	7/3	89	7.5	1.08	18	k 51.7 (0.29) k 69.4 (0.74) sA 160.3 (1.20) i k 68.3 (0.53) sA 161.0 (1.12) i	i 154.2 (1.14) sA 55.8 (0.42) k
9	8/2	85	7.4	1.07	18	g 13.2 k 51.5 (1.56) k 62.2 (-) sA 161.2 (1.20) i g 12.5 k 56.0 (0.29) sA 161.2 (0.99) i	i 154.6 (0.12) sA 35.3 (0.12) k 10.1 g

10	9/1	96	7.7	1.12	19	g 14.1 k 51.6 (2.21) k 56.4 (-) sA 157.7 (1.02) i g 12.0 sA 158.3 (0.94) i	i 151.9 (0.90) sA 8.1 g
11	10/0	81	8.2	1.12	19	g 14.5 k 57.1 (3.45) sA 157.2 (0.90) i g 14.0 sX 44.2 (0.93) sA 156.4 (0.87) i	i 149.4 (0.89) sA 18.9 (0.63) sX 8.8 g

a overlapped peak

Table II. Cationic Copolymerization of 6-3 with 15-8 (polymerization temperature, 0°C; polymerization solvent, methylene chloride; $[M]_o=[6-3]+[13-8]=0.205-0.358M$; $[M]_o/[I]_o=20$; $[(CH_3)_2S]_o/[I]_o=10$; polymerization time, 1hr) and Characterization of the Resulting Copolymers. Data on first line are from first heating and cooling scans. Data on second line are from second heating scan.

Sample No.	[15-8]/[6-3] (mol/mol)	Polymer yield(%)	$Mn \times 10^{-3}$ GPC	Mw/Mn GPC	D P	phase transitions (°C) and corresponding enthalpy changes (kcal/mru) heating	cooling
1	0/10	87	5.9	1.04	21	g 61.3 s_X 68.8 (0.19) n 102.9 (0.12) i g 60.0 n 102.9 (0.10) i	i 97.6 (0.10) n 51.9 g
2	1/9	86	5.4	1.12	18	g 55.1 s_X 60.1 (0.44) Ch 96.8 (0.091) i g 53.0 Ch 96.8 (0.11) i	i 91.8 (0.10) Ch 42.3 g
3	2/8	85	5.6	1.14	18	g 43.2 s_X 51.4 (0.17) Ch 90.6 (0.98) i g 41.3 Ch 90.1 (0.09) i	i 85.4 (0.10) Ch 37.1 g
4	3/7	83	6.2	1.12	18	g 33.9 s_X 39.3 (0.13) s_A 106.3 (0.54) i g 31.5 n 105.6 (0.41) i	i 97.8 (0.40) n 26.5 g
5	4/6	69	6.2	1.15	17	g 29.8 k 48.9 (0.37) s_A 114.4 (0.65) i g 26.3 s_A 114.0 (0.56) i	i 106.3 (0.56) s_A 20.8 g
6	5/5	82	6.4	1.11	17	g 23.4 s_X 48.6 (0.43) s_A 116.0 (0.92) i g 21.4 s_A 115.3 (0.80) i	i 107.4 (0.80) s_A 15.8 g
7	6/4	84	6.7	1.08	17	g 19.4 k 46.5 (0.45) s_A 117.4 (1.18) i g 18.2 s_A 116.5(0.95) i	i 108.7 (0.92) s_A 12.4 g
8	7/3	78	7.9	1.11	19	g 16.4 k 43.1 (0.05) s_A 119.2 (1.19) i g 14.8 s_A 118.7 (1.01) i	i 109.9 (1.00) s_A 10.3 g
9	8/2	77	7.8	1.10	18	g 15.0 s_X 23.9 (0.04) s_C^* 64.1 (0.04) s_A 114.5 (1.15) i g 14.1 s_X 37.4 (0.06) s_C^* 64.3 (0.05) s_A 113.0 (1.00) i	i 104.9 (1.01) s_A 59.9 (0.05) s_C^* 9.5 g
10	9/1	77	9.5	1.10	20	g 16.2 s_X 40.7 (0.14) s_C^* 88.2 (0.09) s_A 114.3 (1.16) i g 14.1 s_X 37.4 (0.06) s_C^* 88.1 (0.11) s_A 113.2 (0.99) i	i 105.5 (0.99) s_A 83.8 s_C^* (0.13) 28.3 (0.07) s_X 9.95 g

11   10/0   77   8.6   1.08   18

g 16.7 s_X 55.2 (0.13) s_{C^*} 93.4 (0.17) s_A 104.7 (1.10) i

g 16.1 s_X 53.7 (0.13) s_{C^*} 92.1 (0.15) s_A 103.7 (0.96) i

l 95.7 (0.93) s_A 86.3 (0.14) s_{C^*} 45.9 (0.12) s_X 13.6 g

x CH$_2$=CH   + y CH$_2$=CH   1) CF$_3$SO$_3$H, (CH$_3$)$_2$S   H-(CH$_2$-CH)$_x$-(CH$_2$-CH)$_y$-OCH$_3$
         | | CH$_2$Cl$_2$
         O   O   2) CH$_3$OH, NH$_4$OH
      (CH$_2$)$_n$ (CH$_2$)$_8$

CN   C=O
                O
                |
                *—Cl
                *

Scheme I

Figure 1

Poly[(6-11)-co-(15-8)]X/Y
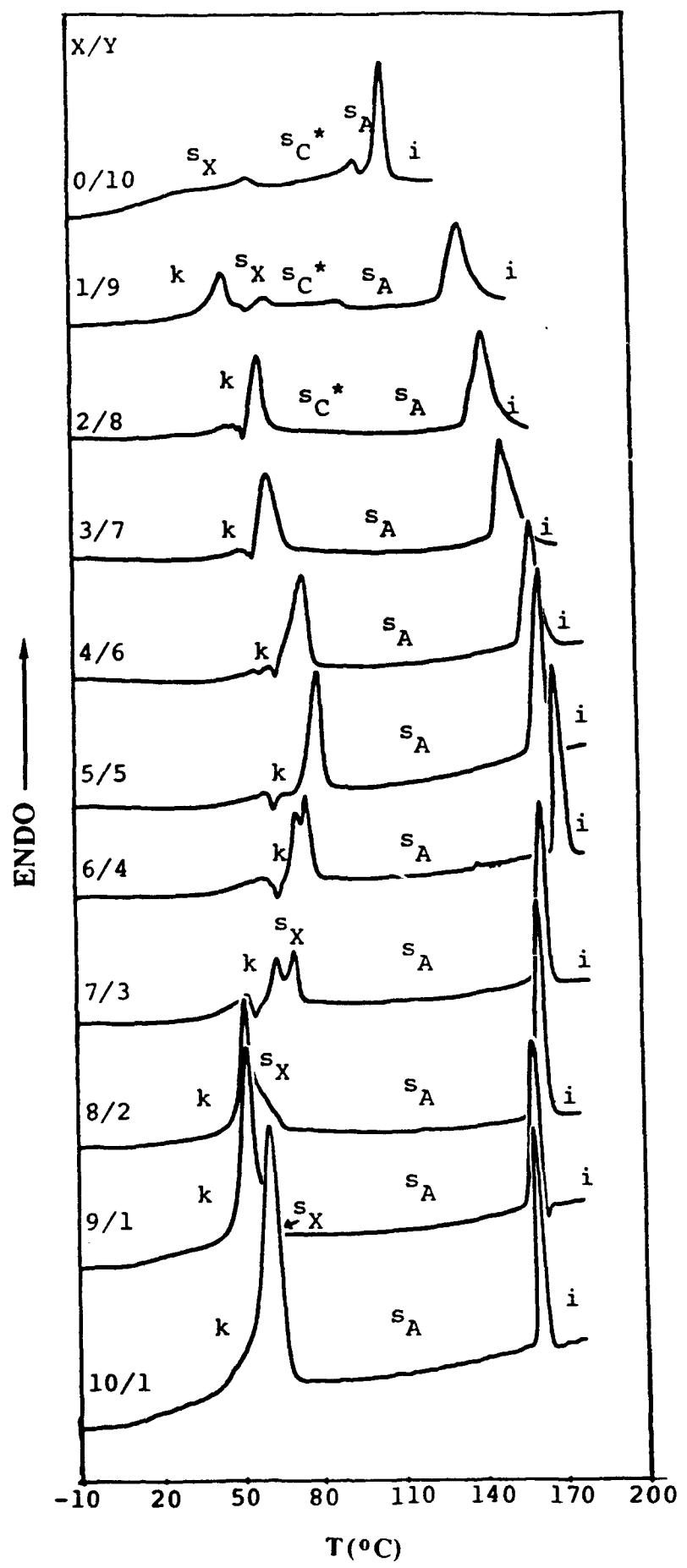
Figure 2a

Poly[(6-11)-co-(15-8)]X/Y
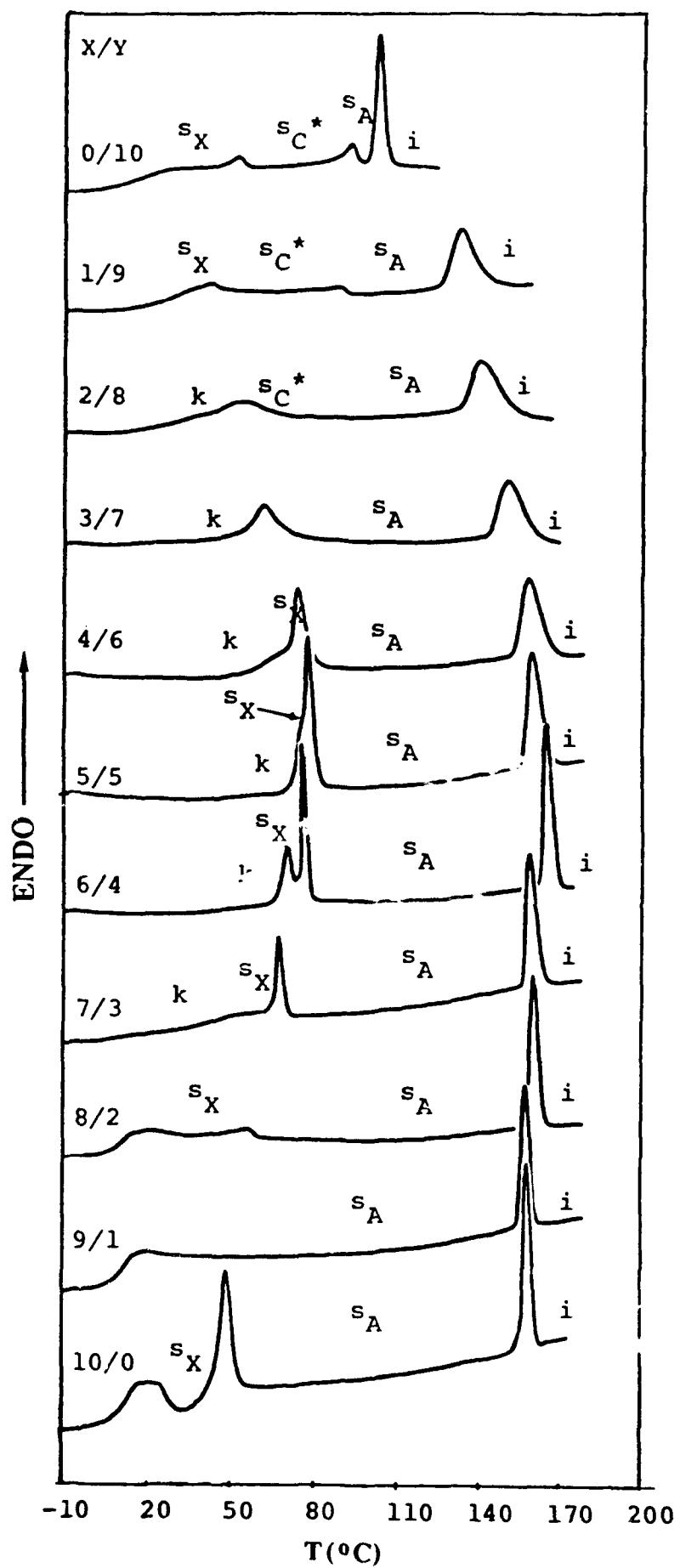
Figure 2b
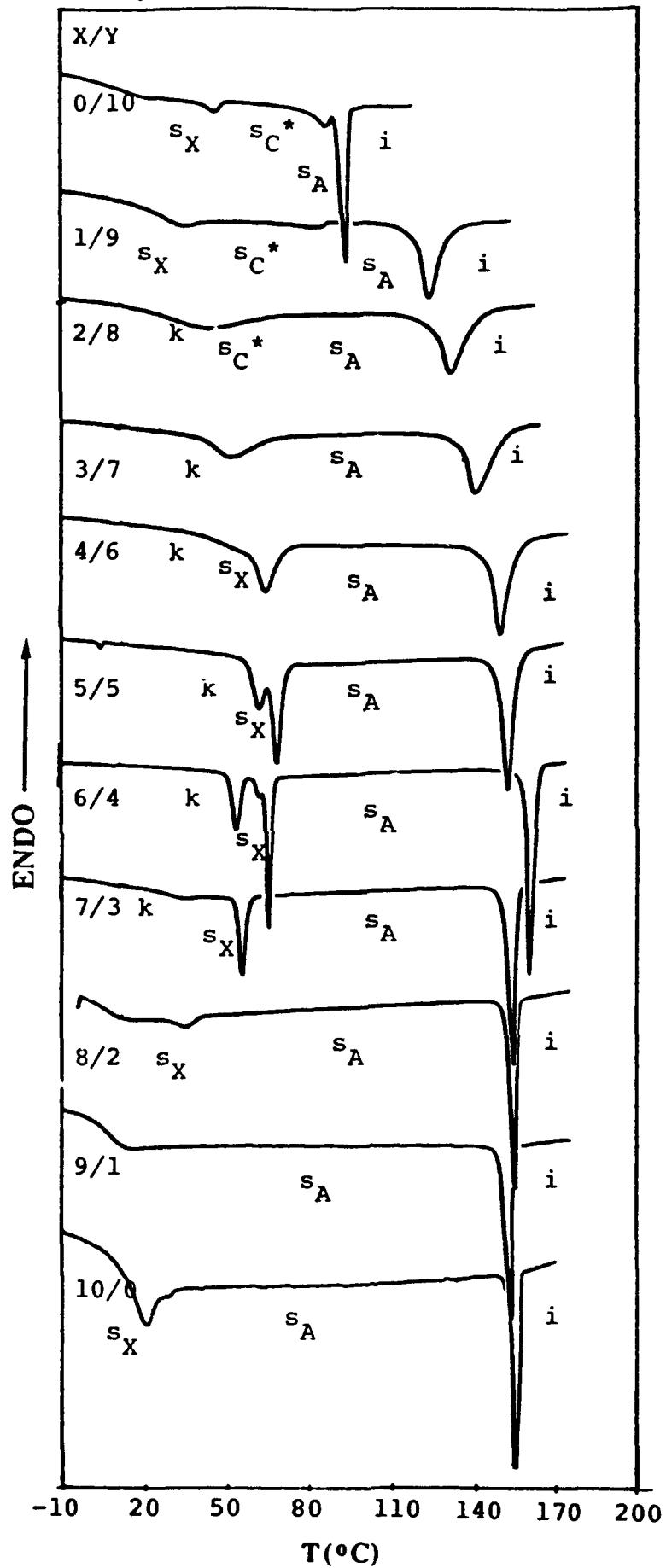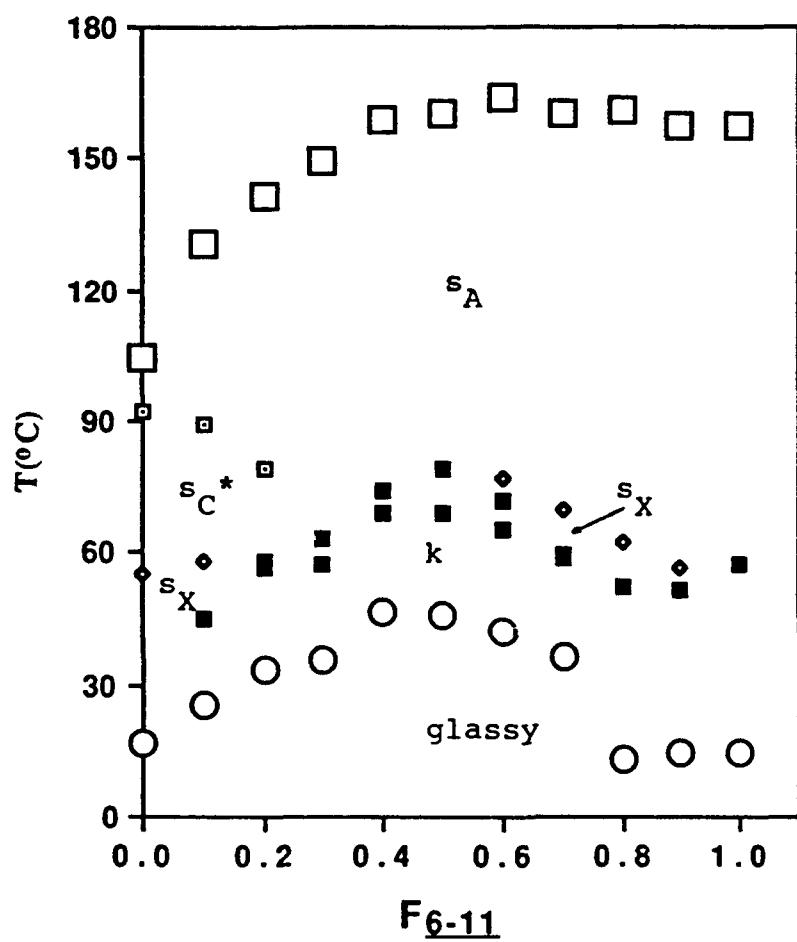
Figure 2c

Figure 3a
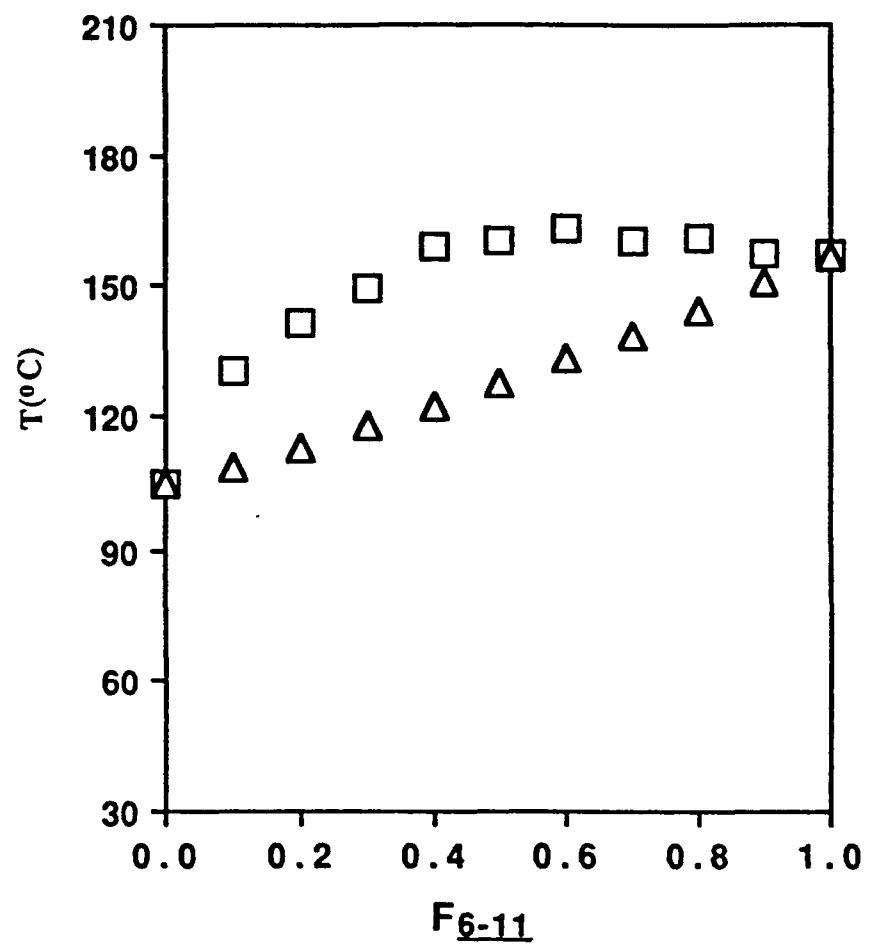
Figure 3b
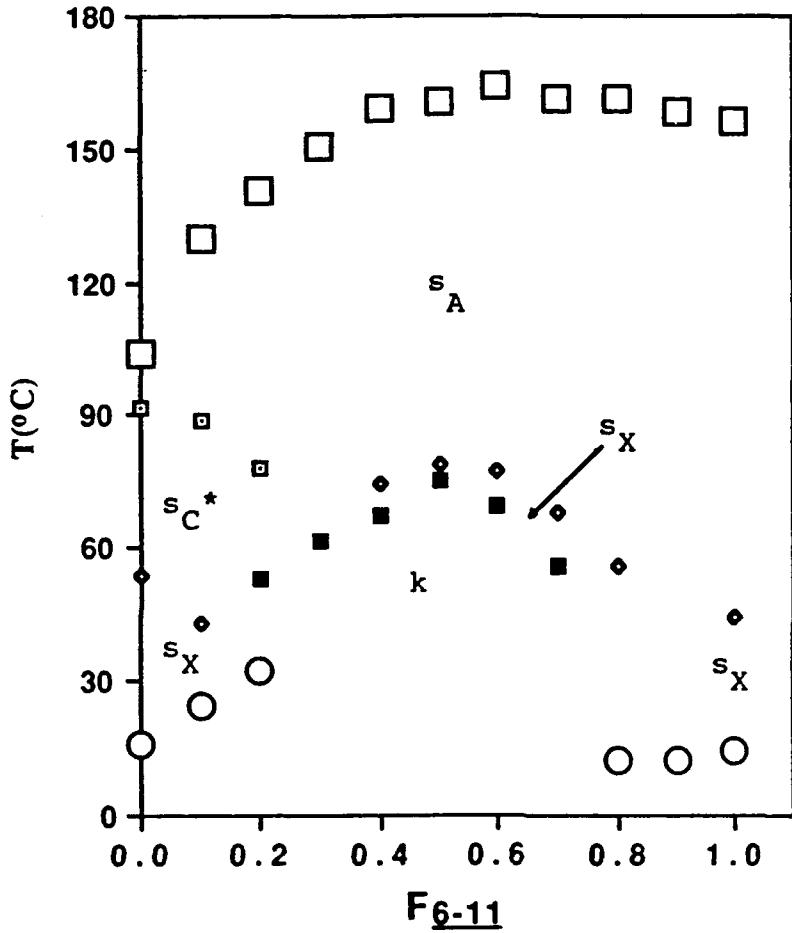
Figure 3c
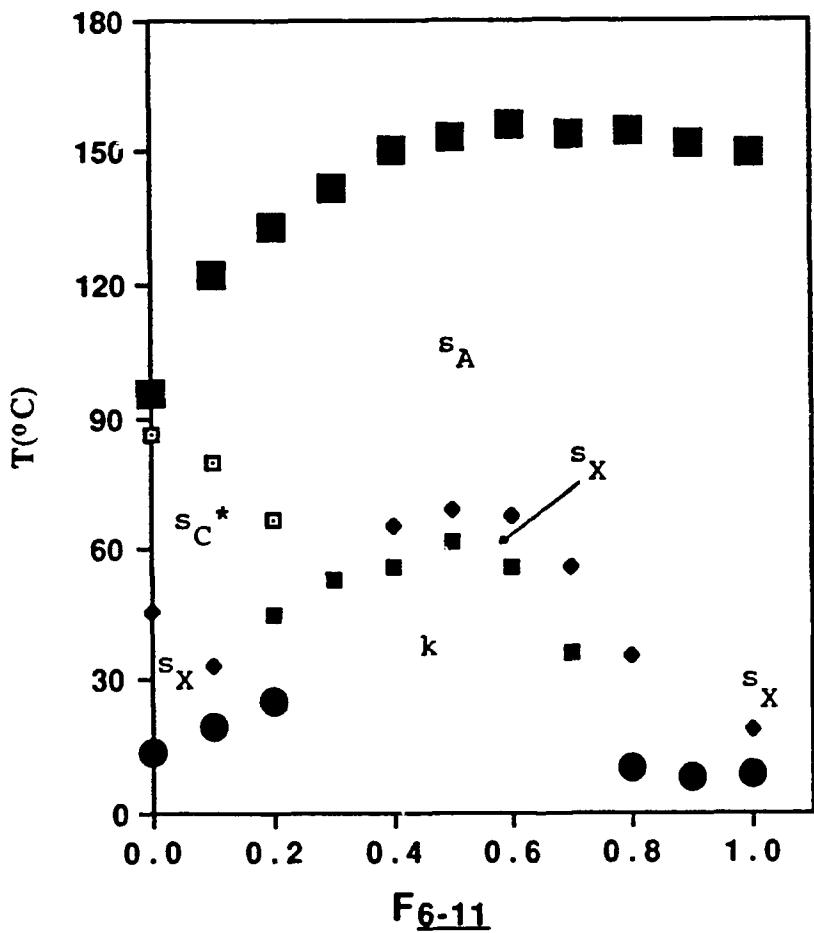
Figure 3d
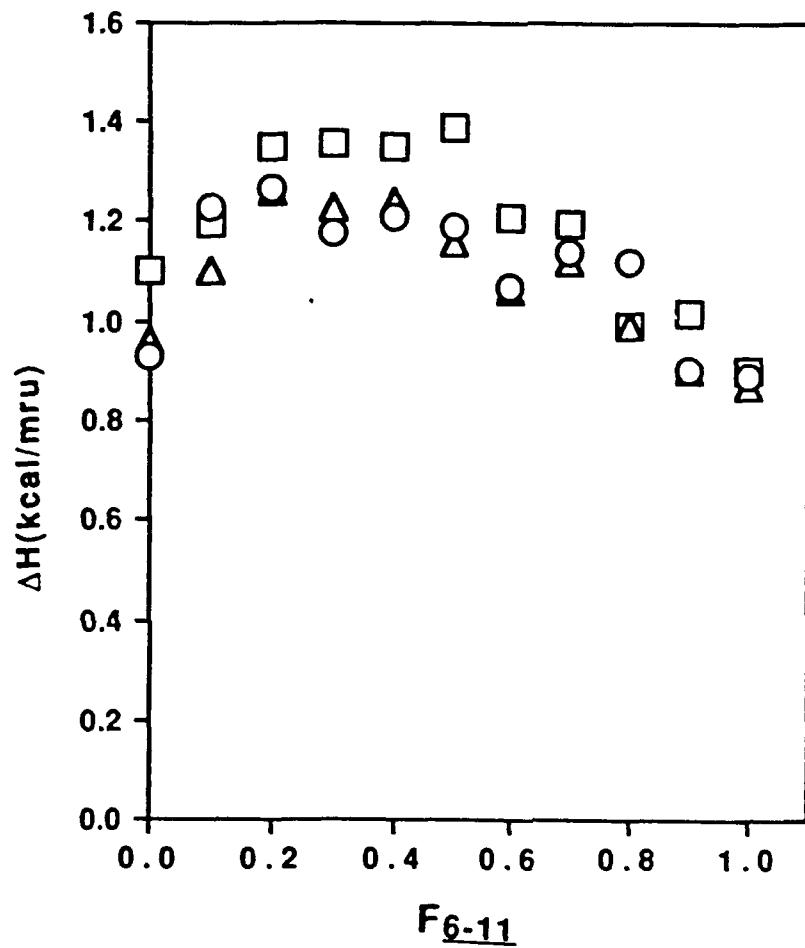
Figure 3e
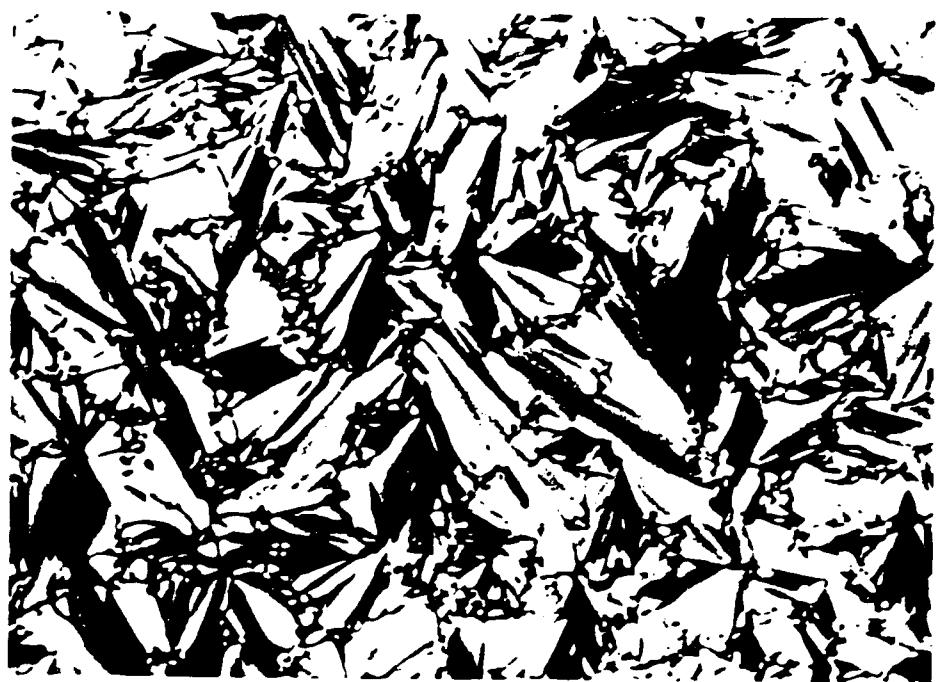
Figure 4a
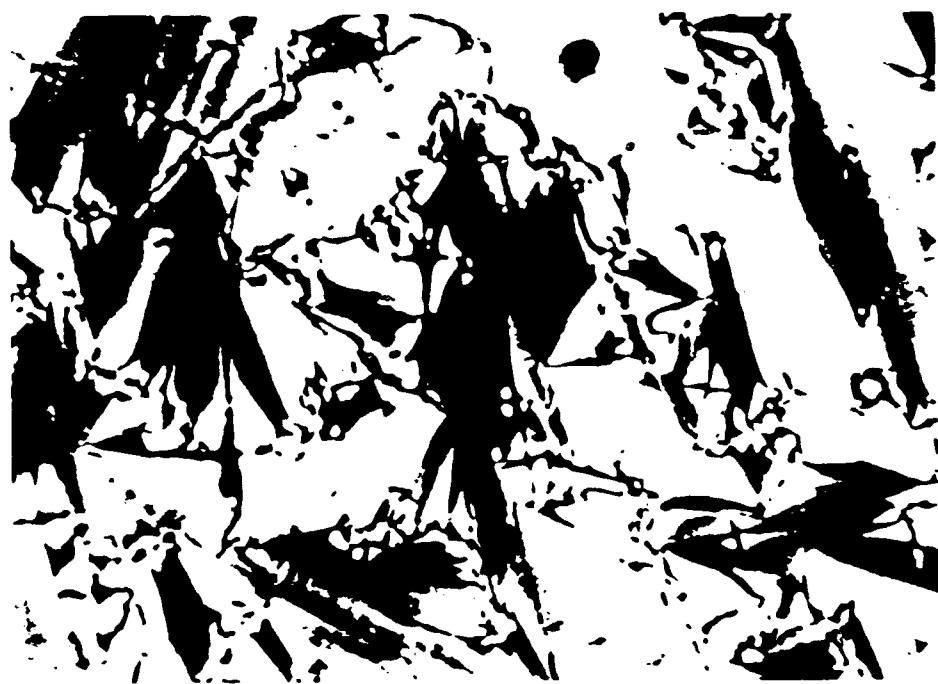
Figure 4b

Poly[(15-8)-co-(6-3)]X/Y
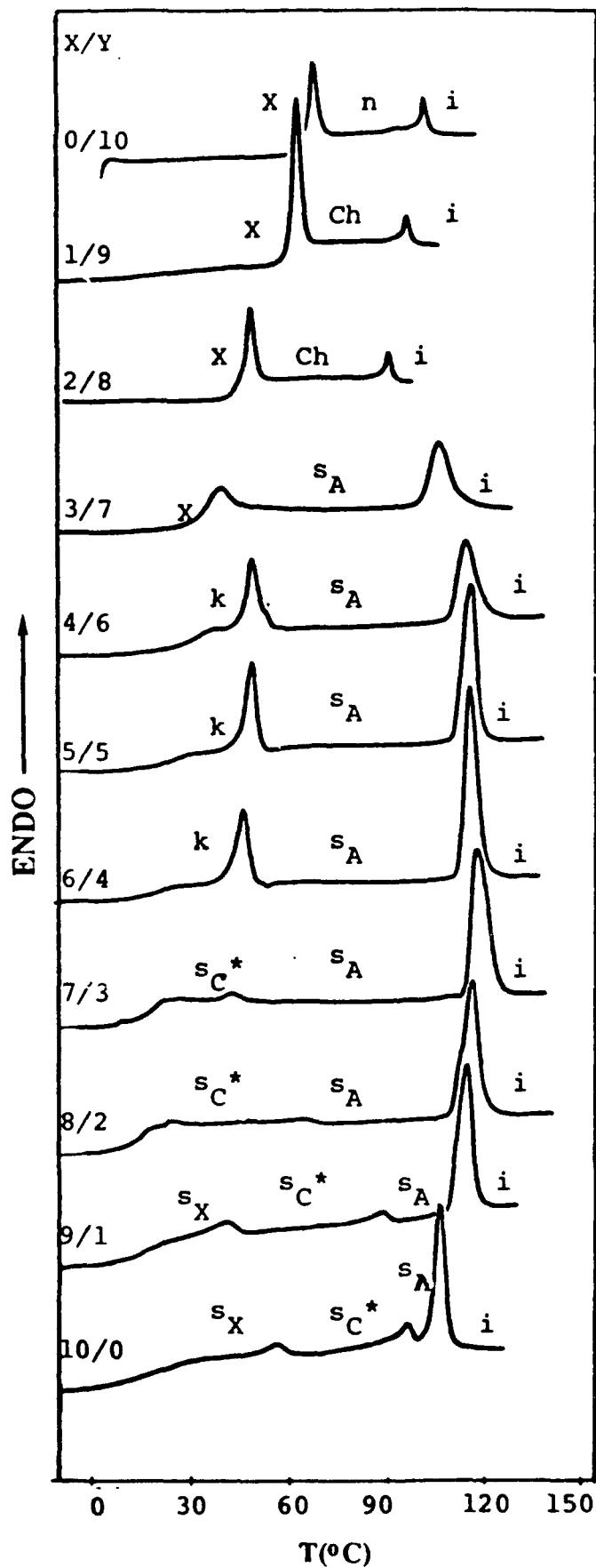
Figure 5a

Poly[($\underline{15\text{-}8}$)-co-($\underline{6\text{-}3}$)]X/Y
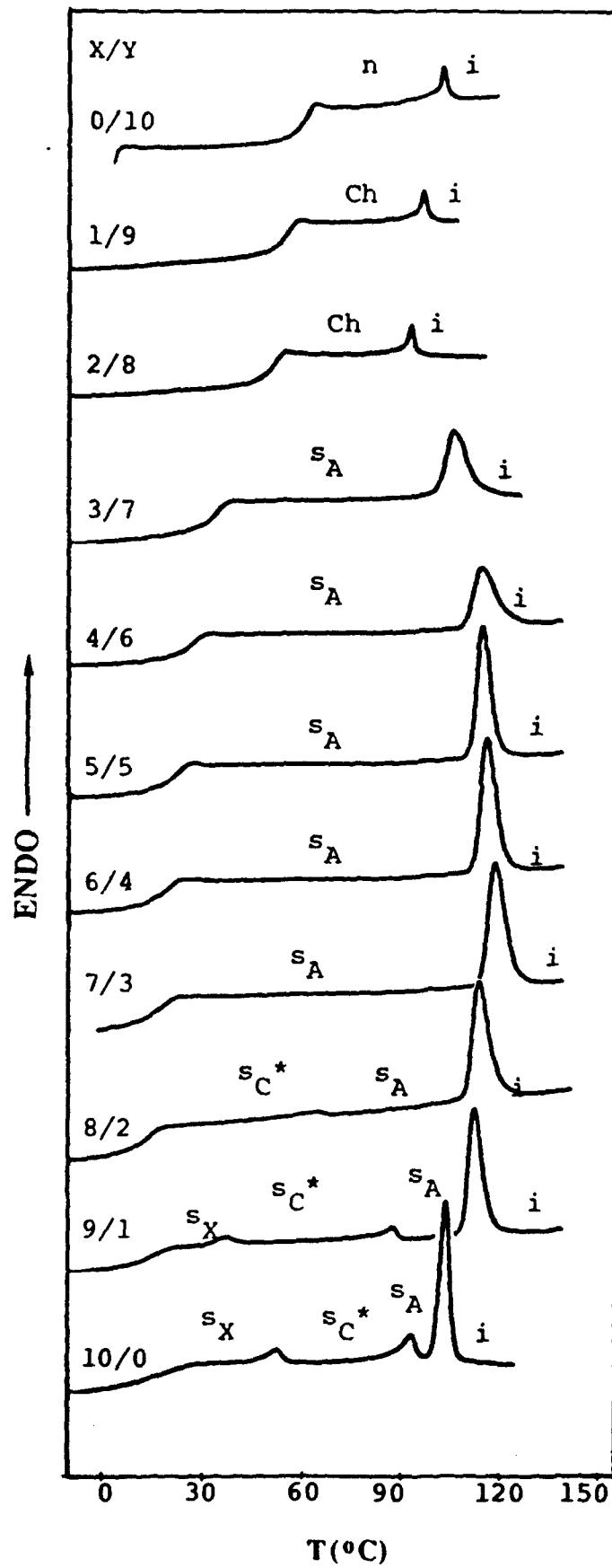
Figure 5b

Poly[(**15-8**)-co-(**6-3**)]X/Y
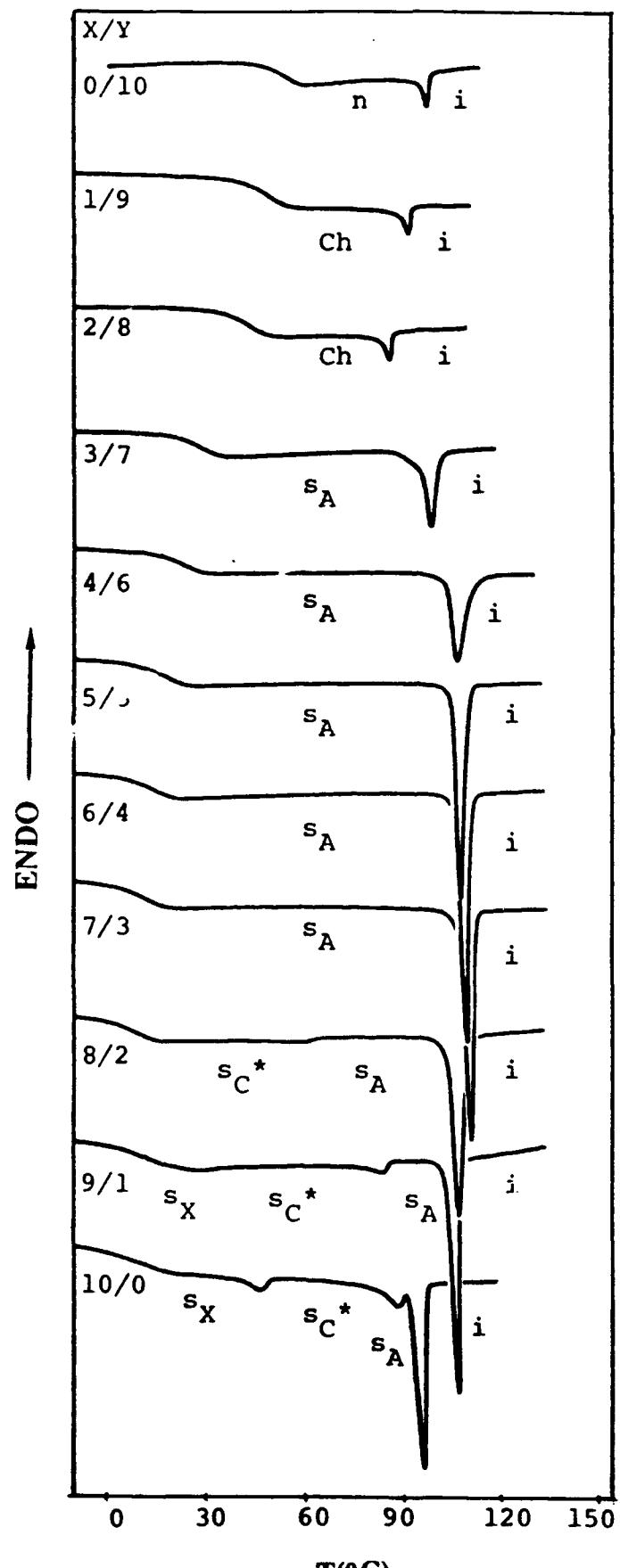
Figure 5c
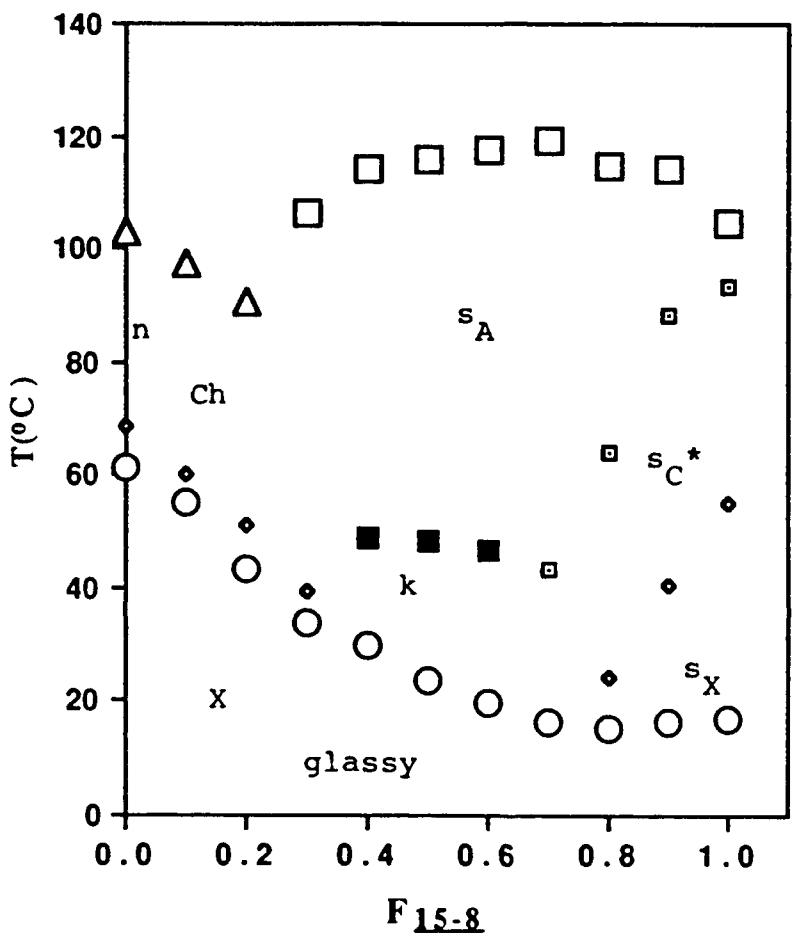
Figure 6a
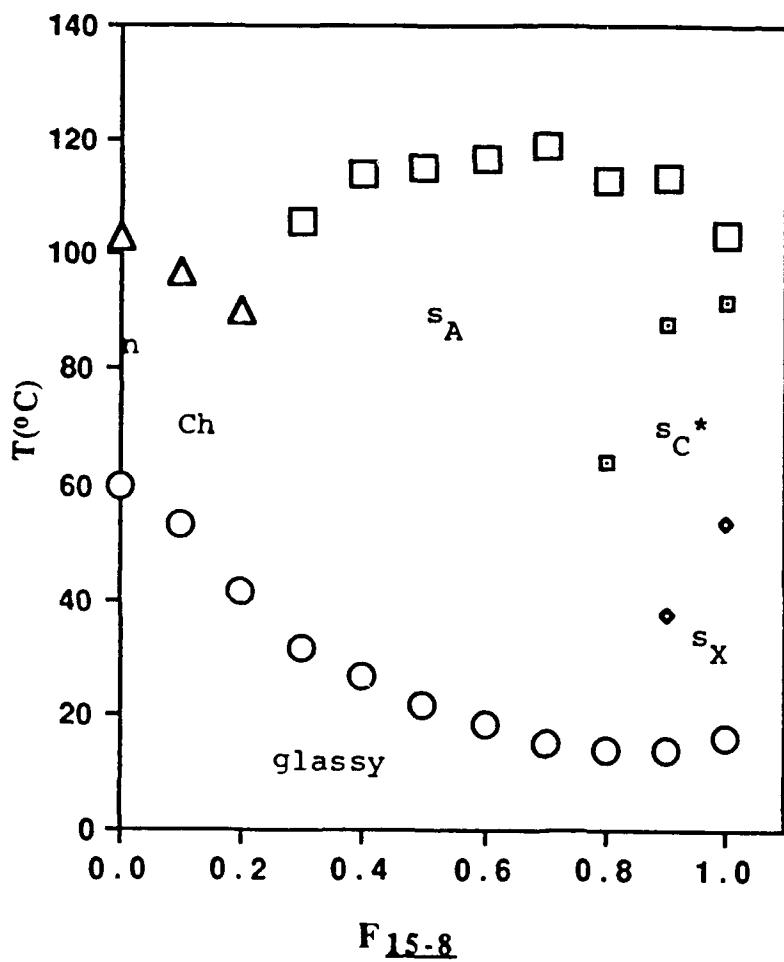
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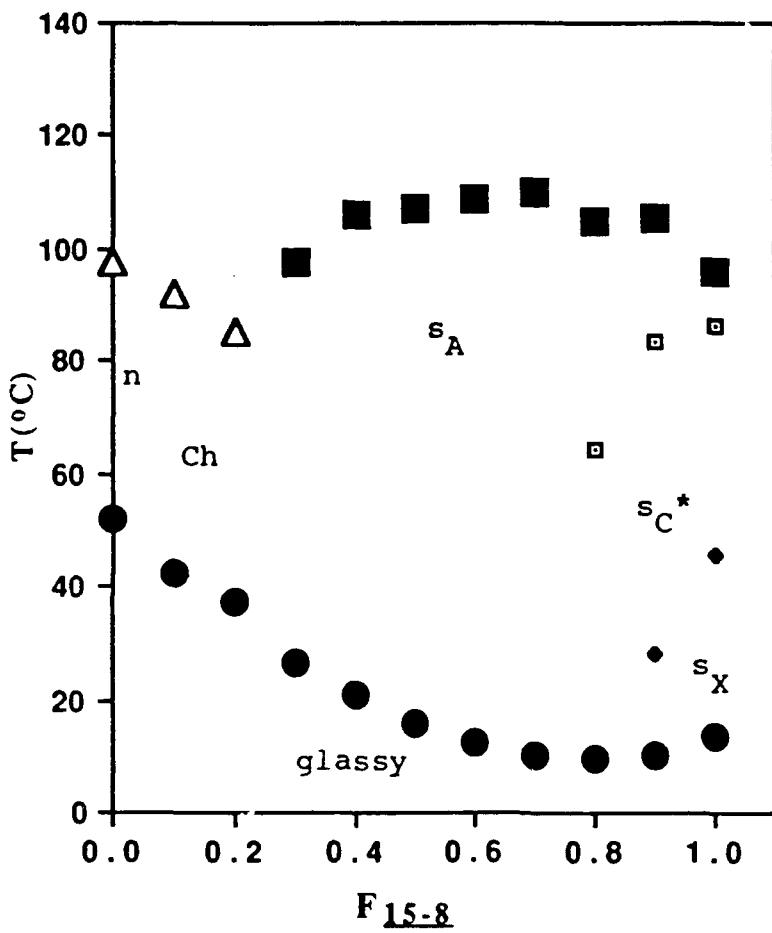
Figure 6c

Figure 6d

Figure 7